

3,522,042

PRESENSITIZED DIAZO MATERIAL FOR THE PREPARATION OF PRINTING PLATES

Henning H. Borchers, Mountainside, and Thomas N. Gillich, Berkeley Heights, N.J., and Fritz Uhlig, Wiesbaden-Biebrich, Germany, assignors, by direct and mesne assignments, to Azoplate Corporation, Murray Hill, N.J.

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8 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to a presensitized material for use in the preparation of printing plates and which comprises an aluminum support having a first layer thereon containing a water-soluble salt of a para-diazodiphenylamine, and a second water-insoluble layer on the first layer, the second layer containing more than 50 percent by weight of at least one light-sensitive para-benzoquinone diazide or para-benziminoquinone diazide.

The materials heretofore known which have been photosensitized by a water-soluble salt of a para-diazodiphenyl amine, or of a para-diazodiphenyl amine derivative obtained therefrom by substitution or condensation with an aldehyde, in addition to many advantages, also have the advantage that they can be developed with water or aqueous liquids which are completely free from organic solvents. This advantage can be fully exploited only in the case of moderately large sizes, up to about the double size of a usual sheet of note paper. With an increase in the size, the fingerprint sensitivity connected with the considerable water-solubility has proved disadvantageous since handling such larger sizes is almost impossible without damaging the reproduction layer. Independently of the formation of fingerprints, processing this known printing plate material under moist, particularly under moist and warm, climatic conditions is difficult since the gelatin layer of the film material serving as the reproduction original, under such conditions, accepts much moisture and, during contact exposure, begins to dissolve the water-soluble light-sensitive layer of the printing plate.

In an attempt to overcome this drawback of the materials photosensitized with water-soluble diazo compounds, the reproduction layer has been coated with a water-insoluble coating consisting substantially of a resin capable of being plasticized by means of organic solvents, but this effort has resulted in presensitized printing plate material which can not be developed with aqueous solutions containing no organic solvent and thus is undesirable in many respects.

A material now has been found which, by means of a water-insoluble coating, is rendered insensitive to fingerprints and is useful even under moist and warm climatic conditions. Furthermore, the material is developable with water or pure aqueous solutions, if more than one half of the weight of the coating consists of at least one water-insoluble, light-sensitive diazo compound having a parabenzoquinone diazide structure or a para-benziminoquinone diazide structure. The material also is superior to material not having such a coating in that higher runs can be achieved with printing plates prepared therefrom. This advantage probably is based upon the fact that a reaction occurs between the light-sensitive substances of both layers, upon exposure to light.

In the preparation of printing plate material according to the invention, the layer which contains the water-soluble light-sensitive diazonium salt and which is applied

as an aqueous solution to the aluminum support, is coated with the second water-insoluble light-sensitive layer containing at least one parabenzoquinone diazide or parabenziminoquinone diazide from a solution substantially free from water (i.e. containing less than 1 percent by weight of water in the solvent). The benzoquinone diazides and benziminoquinone diazides used in accordance with the invention for the formation of the coating are known and also their use as light-sensitive substances in the material for the preparation of printing plates is known, e.g. from German Pats. Nos. 901,500; 960,335; 1,053,930; 1,104,824; 1,003,576; and 1,075,950. If such quinone diazides are included as the light-sensitive substance in only one reproduction layer of a printing plate material, such material has the disadvantage that its exposed layer parts are also attacked by the developer solutions, particularly in the case of higher room temperatures and longer development periods.

In addition to the light-sensitive benzoquinone diazide or benziminoquinone diazide compound, the coating may contain, in known manner, additives, such as resins, plasticizers, activators, pigments, and dyestuffs, even such dyestuffs as are indicators. The total weight of all additives should be less than that of the light-sensitive benzoquinone diazide or benziminoquinone diazide compound. If the coating contains more than one of the light-sensitive compounds, the sum of their weights should be more than half of the total weight of the layer. Suitable resins are, for example, epoxy resins, phthalic, alkyd, maleic, polyvinyl, polyacryl, polyvinyl acetate, melamine, urea, and chlorinated rubber resins. Suitable dyestuffs are, for example, azo dyes, triphenylmethane dyes, and phthalocyanines.

Prior to the application of the water-soluble light-sensitive layer, the aluminum support advantageously is, as is known, subjected to a mechanical, chemical or electrochemical pretreatment. Crude rolled aluminum, for example is cleaned with a hot alkali phosphate or alkali carbonate solution or with a solution containing nitric acid, nitrate, chromate, hydro-peroxide or another suitable oxidizing agent, or roughened by brushing or is electrolytically oxidized. Prior to the application of the water-soluble light-sensitive layer, the aluminum support also may be provided with a layer which improves the adhesive properties thereof, e.g. a layer of silicate, a polyacrylic acid or a phosphonic acid.

For the formation of the water-soluble light-sensitive layer, there are employed the known salts of para-diazodiphenyl amine or of the derivatives of para-diazodiphenyl amine which carry substituents at one or both phenyl nuclei. Such diazonium salts may be present as double salts with metal salts, e.g. with zinc or cadmium salts, or as metal salt-free salts. Preferably employed are the salts in the form of their condensation products with formaldehyde in the metal salt-free form. The preparation of different kinds of condensation products and of light-sensitive layers containing such products, inter alia, is described in German Pats. Nos. 1,142,871; 1,154,123; 1,138,399; 1,138,400; and 1,138,401; in French Pat. No. 1,321,460, and in the two French patents of addition Nos. 83,774 and 73,775. In addition to one or more of the aforementioned light-sensitive substances, the water-soluble reproduction layer may contain, in known manner, one or more of the aforementioned additives.

As stated above, the use of benzoquinone diazides and benziminoquinone diazides as the light-sensitive substance, with the above-described disadvantages, is known for the preparation of presensitized printing plate material. When using the quinone diazides in accordance with the present invention, such disadvantages do not occur, however. It happens instead that the second layer consisting completely or substantially of quinone diazides

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not only decreases the sensitivity to moisture but also, surprisingly, the developability with pure aqueous solutions is retained. It is also surprising that, as a result of the second layer, the printing run is substantially higher, i.e. at least doubled.

The invention will be further illustrated by reference to the following specific examples, in which quantities are by weight:

EXAMPLE 1

A bright rolled aluminum foil which was cleaned by rinsing it for 5 minutes with a trisodium phosphate solution at a temperature of 80° C. and immersing it for 3 minutes in a 5 percent sodium silicate solution at a temperature of 85° C. was dried and coated with a 1 percent aqueous solution of a zinc chloride salt of a diazo compound which had been prepared from 1 mole of 4-diazodiphenylamine and 1 mole of formaldehyde, by condensation in sulfuric acid, and dried. In another operation, a solution of:

0.8 percent of 1-[(4'-methylbenzene-1'-sulfonyl)-imino]-2-(2'',5''-dimethyl-phenylamino - sulfonyl) - benzoquinone-(1,4)-diazide-(4), and
99.2 percent of ethylene glycol monomethyl ether

was applied to the foil thus sensitized and dried. The foil was then cut into large printing plate sizes.

The presensitized printing plates obtained were insensitive to fingerprints and tropical working conditions and could be stored in the dark for many months.

For the preparation of a printing plate, exposure to light was performed under a photographic negative and the exposed layer was wiped over with a cotton pad soaked with water containing 3 percent of trisodium phosphate and 1 percent of sodium silicate. The light-sensitive layers were thereby removed in the areas not struck by light.

The exposed areas were not attacked by the developer even at working temperatures of about 35° C. After rinsing with water, the printing plate thus prepared was inked up with greasy ink. Long runs could be achieved therewith in a printing machine.

For comparison, a similar aluminum foil was pretreated in the same manner and provided with the light-sensitive layer of the same water-soluble diazo compound, but the water-insoluble layer was not applied. The printing plate thus prepared was sensitive to fingerprints and involved processing difficulties in a humid atmosphere.

EXAMPLE 2

An electrolytically-roughened aluminum tape which had been pretreated with a 1 percent polyacrylic acid solution was sensitized as in Example 1 with an aqueous solution of a condensation product of 4-diazodiphenylamine and formaldehyde. It was then coated with a solution of:

0.5 percent of 1-[(4'-methylbenzene-1'-sulfonyl)-imino]-2,5-diethoxy-benzoquinone-(1,4)-diazide-(4), and
99.5 percent of ethylene glycol monoethyl ether,

dried, and cut into sizes.

For the preparation of a printing plate, exposure to light was performed under a negative and development was effected with a 3 percent orthophosphoric acid solution, whereupon inking up with greasy ink was performed.

EXAMPLE 3

An electrolytically-roughened aluminum tape which had been pretreated in known manner with a phosphonic acid solution was sensitized with an aqueous solution of 0.8 percent of a crude condensate prepared from 3-methoxy-diphenylamine-4-diazonium chloride and paraformaldehyde by condensation in phosphoric acid (the solution containing the phosphoric acid used for condensation) and 0.1 percent of polyvinyl acetate, and then was provided with a coating from a solution of:

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0.53 percent of 1-[(4'-methylbenzene-1'-sulfonyl)-imino]-2-(2''-ethylphenylaminosulfonyl)-benzoquinone - (1,4)-diazide-(4),

0.30 percent of polyvinyl acetal, viscosity 4 to 6 centipoises at 20° C. in a 2 percent solution in methylene dichloride, e.g. Mowital F40 (registered trade mark of Farbwerke Hoechst),

0.1 percent of 4'-acetamino-4-dimethylamino-azobenzene, and

99.16 percent of methyl glycol acetate,

The coating then was dried.

For the preparation of a printing plate, exposure to light was performed under a negative and development was with an aqueous solution containing 1.2 percent of phosphoric acid, 3 percent of sodium sulfate, and 1.6 percent of magnesium nitrate, whereupon inking up with greasy ink was performed.

EXAMPLE 4

An aluminum foil was pretreated, as in Example 1, and sensitized with the same aqueous solution. A solution of

0.8 percent of benzoquinone-(1,4)-diazide-(4)-2-(N- β -naphthyl)-sulfonamide, and
99.2 percent of ethylene dichloride

was then applied and dried.

The procedure for the preparation of a printing plate was the same as in Example 1.

EXAMPLE 5

A mechanically roughened aluminum tape was chemically pretreated in a phosphonic acid bath and sensitized with a 0.6 percent aqueous solution of a condensation product of paraformaldehyde and diphenylamine-4-diazonium chloride. A solution was then coated thereon containing:

0.6 percent of 1-[(4'-methylbenzene-1'-sulfonyl)-imino]-2-(4''-methoxyphenylamino - sulfonyl) - benzoquinone-(1,4)-diazide-(4),

0.3 percent of epoxy resin (melting point at about 70° C., epoxide equivalent weight about 500 and hydroxyl value about 0.3, e.g. the product available under the trade name "Epikote" 1001 of Shell), and

99.1 percent of ethylene glycol acetate ethyl ether.

The procedure for the preparation of a printing plate was the same as in Example 1.

EXAMPLE 6

An aluminum foil was pretreated, as in Example 3, and sensitized with the same aqueous diazo solution. The foil was then coated with a solution of:

0.4 percent of benzoquinone-(1,4)-diazide-(4)-2-sulfonic acid-(ethylphenyl)-amide, and
99.6 percent of 1,1,2-trichloroethane

and dried.

The procedure for the preparation of a printing plate was the same as in Example 1.

The same procedure of Example 1 was repeated with the exception that as the water-insoluble quinone diazide there was used benzoquinone-(1,4)-diazide-(4)-2-(N- α -naphthyl- β -ethoxy)-sulfonamide. Similar results were obtained.

EXAMPLE 7

A presensitized printing plate was prepared in accordance with Example 3 with the exception that a sensitizing solution of:

0.6 percent of diphenylamine-4-diazonium-chloride, and
99.4 percent of methyl glycol acetate,

and a coating solution of:

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0.8 percent of the benzoquinone diazide of Example 3,
0.5 percent of polyvinyl acetal as in Example 3,
0.1 percent of polyvinyl acetate, and
98.6 percent of methyl glycol acetate
were applied.

It will be obvious to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the spirit thereof, and the invention includes all such modifications.

What is claimed is:

1. A presensitized printing plate comprising an aluminum support, a first layer on the support comprising a light sensitive water-soluble salt of at least one compound selected from the group consisting of a para-diazodiphenylamine and a para-diazodiphenylamine condensed with an aldehyde, and a second water-soluble layer on the first layer, the second layer containing at least about 50 percent by weight based upon the total weight of the said second layer of at least one light-sensitive compound selected from the group consisting of a para-benzoquinone diazide and a para-benziminoquinone diazide the light decomposition products of the light-sensitive ingredients in both layers being insoluble in an aqueous developer solution.

2. A presensitized printing plate according to claim 1 in which the second layer contains 1-[(4'-methylbenzene-1' - sulfonyl) - imino] - 2 - (2'',5'' - dimethyl - phenylamino-sulfonyl)-benzoquinone-(1,4)-diazide-(4).

3. A presensitized printing plate according to claim 1 in which the second layer contains 1-[(4'-methylbenzene-1' - sulfonyl) - imino] - 2 - (2'' - ethyl - phenylamino - sulfonyl)-benzoquinone-(1,4)-diazide-(4).

4. A presensitized printing plate according to claim 1 in which the second layer contains benzoquinone-(1,4)-diazide-(4)-2-sulfonic acid-(ethylphenyl)-amide.

5. A process for making a printing plate which comprises exposing light-sensitive coatings on an aluminum support to light under a master and developing the said coatings with an aqueous developer to remove the unexposed areas of the said coatings, the coating comprising a first layer including a water-soluble salt of at least one

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compound selected from the group consisting of a para-diazodiphenylamine and a para-diazodiphenylamine condensed with an aldehyde, and a second water-insoluble layer on the first layer, the second layer containing at least about 50 percent by weight based upon the total weight of the said second layer of at least one light-sensitive compound selected from the group consisting of a para-benzoquinone diazide and a para-benziminoquinone diazide.

6. A process according to claim 5 in which the second layer contains 1-[(4'-methyl-benzene-1'-sulfonyl)-imino]-2-(2'',5''-dimethyl-phenylamino-sulfonyl) - benzoquinone-(1,4)-diazide-(4).

7. A process according to claim 5 in which the second layer contains 1-[(4'-methyl-benzene-1'-sulfonyl)-imino]-2-(2''-ethyl-phenylamino-sulfonyl)-benzoquinone - (1,4) - diazide-(4).

8. A process according to claim 5 in which the second layer contains benzoquinone-(1,4)-diazide-(4)-2-sulfonic acid-(ethylphenyl)-amide.

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NORMAN G. TORCHIN, Primary Examiner

C. BOWERS, Assistant Examiner

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96—36.3, 49, 75

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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Henning H. Borchers et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 61, "73,775" should read -- 83,775 --.
Column 5, line 6, of claim 1, "water-soluble" should read -- water-insoluble --.

Signed and sealed this 29th day of September 1970.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents